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# Fractality aspects during agglomeration of solid-phase-epitaxy Co–silicide thin films*

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Morphology changes of thin $CoSi_2$ films close to the agglomeration threshold have been investigated by *in situ* scanning tunneling microscopy. Films prior to agglomeration reveal a strong morphology anisotropy where depending on direction the roughness correlation $g(r)$ changes from logarithmic $[g(r)\sim \ln r]$ to power law $[g(r)\sim r^{2c}$ with $c\approx 0.78]$ at short lateral length scales ($r \leqslant 30$ nm). Such an anisotropy reflects the complex nature of diffusion process associated with the original anisotropic substrate surface and the formation of pinhole networks. Annealing above the agglomeration threshold (>600 °C), the pinhole network becomes connected breaking the $CoSi_2$ film into aggregates with a two-dimensional fractal dimension $D\approx 1.66$ which is close to predictions of diffusion limited aggregation within the mean field theory prediction $D=(d^2+1)/(d+1)$ for $d=2$, and invasion percolation models. © *2000 American Vacuum Society.*
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## I. INTRODUCTION

The fabrication and application of metal silicide thin films has been a great success in the field of microelectronics semiconductor technology. As a result, there is much interest in the fabrication of metal silicide thin films (i.e., $CoSi_2$, $TiSi_2$, $NiSi_2$)[1] because of their application in complementary-metal–oxide–semiconductor processes,[2] and microelectronics circuits (gates, contacts, interconnects, etc.).[3] Moreover, their low resistivity makes them important for the formation of self-aligned silicides[4] in ultralarge-scale integrated devices. In many cases the application of silicides in microelectronics is limited by stability problems at high temperature processing because of agglomeration of the film into discrete islands.

A variety of film degradation mechanisms which related to grain size, grain-boundary energy, and silicide interface and surface energy have been proposed.[5] It is suggested that small grain size, small grain-boundary energy, large surface/interface energy, or thicker films may result in better thermal (or more precisely morphological) stability.[5,6] The surface energy in metals is much larger than grain-boundary and interface energy.[7] If metal–silicides share the same property,[6] a large surface energy suggests that thermal grooving would start at the silicide/Si interface rather than at the silicide surface. As a result an increment in the silicide surface energy would not be as efficient as an increment in the silicide/Si interface energy to prevent film agglomeration.[6,8] Therefore, the interface energy can be the key factor which determines the morphological stability of the films.

Furthermore, a $CoSi_2$ film of significant thickness (~70 nm; $CoSi_2$ implanted by $BF_2^+$) could release its high surface energy through Si precipitation (since Si surface has lower energy than the $CoSi_2$ surface) and silicide/Si interface roughness.[6] Silicide/Si interface roughness (e.g., in $CoSi_2$ formed via the nucleation control process associated in some cases with a native oxide on the original Si surface[6,9]) contributes positively to the interfacial energy, and thus to the resistance against agglomeration to a degree that depends on the specific roughness characteristics.[10] In addition, the growth of larger area epitaxial silicides possibly eliminates thermal grooving paths possibly promoting silicide morphological stability.[6,11] On the other hand, in polycrystalline films the agglomeration mechanism can be thermal grooving at grain boundaries. The maximum grain size $L_c$ for which agglomeration cannot occur via this mechanism is given by $L_c\approx 10\tau$ (with $\tau$ the film thickness).[5] This is estimated assuming comparable grain boundary and interface energies of about 1/3 of the surface free energy (e.g., pure metals).[5,7,12]

In the present work we will investigate the morphology characteristics of ultrathin $CoSi_2$ films grown by solid-phase epitaxy (SPE) close to the agglomeration threshold using topology information obtained by scanning tunneling microscopy (STM) and scanning electron microscopy (SEM). The SPE technique involves metal deposition on clean Si which is followed by annealing at elevated temperatures to form epitaxial silicide.[1] Morphology quantification will be performed in terms of a height–height correlation function measurement prior to agglomeration, and two-dimensional fractal analysis by means of the box counting technique after agglomeration has occurred.

## II. EXPERIMENTAL SAMPLE PREPARATION

The Si(111) wafers used in this study were *n* doped with resistivity of ~100 Ω cm, and nominally flat (miscut angle <0.1°). The sample preparation was performed in an ultrahigh vacuum chamber of base pressure $P_b\approx 1\times 10^{-10}$ mbar. Clean Si(111)7×7 reconstructed surfaces were formed by resistive heating at a temperature ~500 °C

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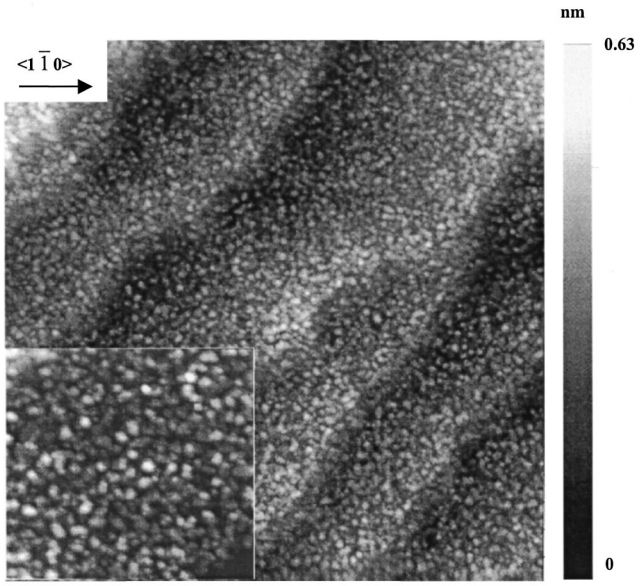


FIG. 1. Co film of 0.5 nm deposited on clean Si(111)7×7 surface held at RT. STM filled state image acquired at 1.55 V bias voltage and 0.16 nA tunnel current. Scan size 200×200 nm. The inset at the right bottom of 50×50 nm scan size depicts the short length scale granular Co morphology.

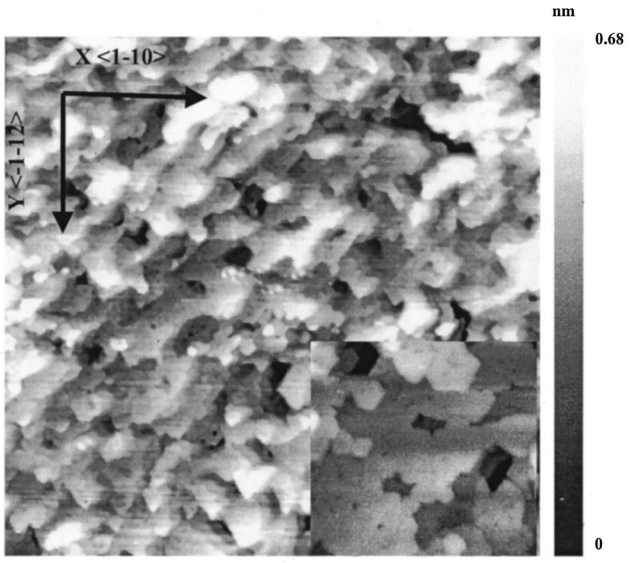


FIG. 2. Annealing of the film in Fig. 1 at 500 °C for 3 min. Large scale image of 500×500 nm scan size where the roughness measurements took place. The inset is a small scan size image of 100×100 nm to show in more detail the film granular. STM empty state images acquired at 1.62 V bias voltage and tunnel current 1.56 nA.

and at a pressure of $\sim 5\times 10^{-10}$ mbar for gas desorption followed by a flash to ~1200 °C for ~1 min. The specimen temperature was determined by infrared pyrometry to better than ±10 °C above 400 °C. Co films of 0.5 nm in thickness were deposited *in situ* by means of e-beam evaporation at a rate 0.1 nm/min on Si(111) samples held at room temperature (RT). The evaporation rate was calibrated by a quartz crystal microbalance to within ~10%. During evaporation the chamber pressure did not exceeded $\sim 5\times 10^{-9}$ mbar. In all stages the samples were imaged *in situ* into an STM (OMICRON) chamber held at a base pressure $\sim 1.5\times 10^{-10}$ mbar. Mechanically cut Pt/Ir STM tips were used for imaging purposes.[13]

## III. MORPHOLOGY ANALYSIS PRIOR TO FILM AGGLOMERATION

Figure 1 shows the topology of the Co/Si films just evaporated on a clean Si(111)7×7 surface. As seen in the STM images the grain size is about ~3 nm. Co atoms react with Si atoms even at room temperature for the first few monolayers of deposited metal.[14,15] Complete surface coverage is possible because of the high surface diffusivity of unreacted Co migrating to regions of unexposed Si surface. The granular structure indicates that the film is not fully reacted to form an epitaxial $CoSi_2$ (the RT Co–Si reaction only takes place locally while no long-range order transport occur by either species, namely, Co and Si).[13,15]

Drastic changes in the surface morphology of the Co/Si film occurs during further annealing at elevated temperature to form $CoSi_2$ as Fig. 2 indicates. Indeed, annealing at 500 °C for 3 min (Fig. 2) leads to the formation of pinholes which are surrounded by stepped epitaxial terraces.[13] The surface morphology is quantified by measurement of the height–height correlation function $g(r)=\langle[h(r)-h(0)]^2\rangle \times(r=x,y)$ along the $x$ and $y$ axis as shown in the STM image of Fig. 2.[14] In each direction ($x$ and $y$), six one-dimensional height profiles $h(r)$ vs $r$ were acquired (at different locations) over a lateral scan size of 500 nm (which is about ten times larger than the average terrace size ~60 nm), followed by computation of $g(r)$ vs $r$ for each profile separately, and finally the average of all six $g(r)$ vs $r$ curves.

The anisotropy of the initial Si(111)7×7 stepped surface will impose anisotropy in the growth of $CoSi_2$ (as Fig. 2 shows in comparison with Fig. 1) along directions running at about 45° from the $x$ and $y$ directions (Fig. 2). Along the $x$ axis ($\langle 1,-1,0\rangle$ direction), a logarithmic behavior of $g(x)$ ($\propto \ln x$) is revealed at short length scales 3–30 nm [Fig. 3(a)]. Saturation appears to commence at larger length scales $x \geqslant 70$ nm, which compare to lateral sizes of epitaxial domains formed in between the network of pinholes. In fact, logarithmic behavior corresponds to roughness exponents $c=0$.[16] The saturated rost mean square (rms) roughness amplitude is $\sigma_x \approx 0.18$ nm. On the other hand, $g(y)$ along the $y$ axis ($\langle -1,-1,2\rangle$ direction) shows a power law behavior $g(y)\propto y^{2c}$ with $c=0.78\pm 0.05$ for lateral length scales $y<20$ nm [Fig. 3(b)], and a saturated rms roughness amplitude $\sigma_y \approx 0.13$ nm at lateral length scales $y \geqslant 30$ nm. The structural change from logarithmic to power law behavior of the correlation functions in the $x$ and $y$ directions indicates, qualitatively, the complex anisotropic character of the $CoSi_2$ growth at short length scales smaller than the terraces (which have a period of 70–100 nm; Fig. 1) of the initial Si(111)7×7 surface. Large roughness exponents close to $c\approx 0.7-1$ indicate a surface diffusive process with a mountain-valley structure developing, while a logarithmic behavior (or alternatively roughness exponent $c\approx 0$) indicates the absence of any surface diffusion.[17]

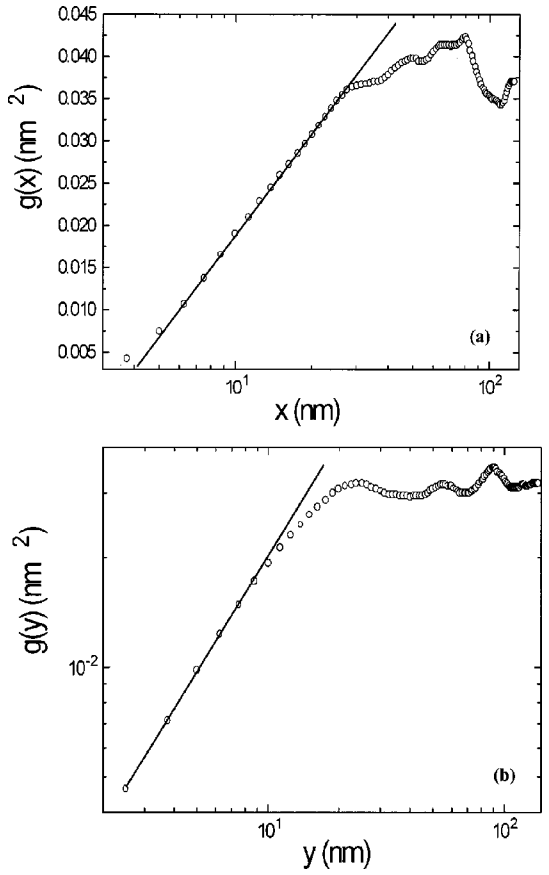


FIG. 3. Schematics of the correlation function $g(r)$ vs $r$ (a) along the $x$ axis. (b) along the $y$ axis. The line indicates the linear fit to measure the roughness exponent $c = 0.78 \pm 0.05$.

The occurrence of pinholes has been related to the transformation of the Co-rich to the Si-rich silicide surface (which has a lower surface energy and possibly drives the process).[15,18] The necessary amount of Si is provided from the Si substrate by bulk outward diffusion to the surface and the subsequent reaction with Co.[13] Our measurements indicate that the associated diffusion process on the silicide surface are rather highly anisotropic resulting in strong directional dependence of the film growth front. In any case, the growth mode of such a system is too complicated to be accounted for solely in terms of simple nonreactive growth models.[17,19] Further studies are necessary in this direction.

## IV. MORPHOLOGY ANALYSIS AFTER FILM AGGLOMERATION

During further annealing of the film at 700 °C for 3 min (Fig. 4), the pinhole network is getting connected breaking up the film into complicated still shape $CoSi_2$ precipitates.[13] The height of these precipitates can be as high as ~10 nm. Further annealing leads to more polygonal shapes (crystallographically oriented) of the $CoSi_2$ precipitates (Fig. 5). Despite the variety of shapes, the polygonal precipitate sides are formed mainly along two preferential orientations: along the substrate Si(111) terraces or $\langle 1\bar{1}0 \rangle$ direction and other two at ~60° and ~120° (threefold symmetry). The dominant surface orientation of the $CoSi_2$ precipitates is the {111} crystallographic plane, which is energetically favorable independently of the matrix orientation.[18]

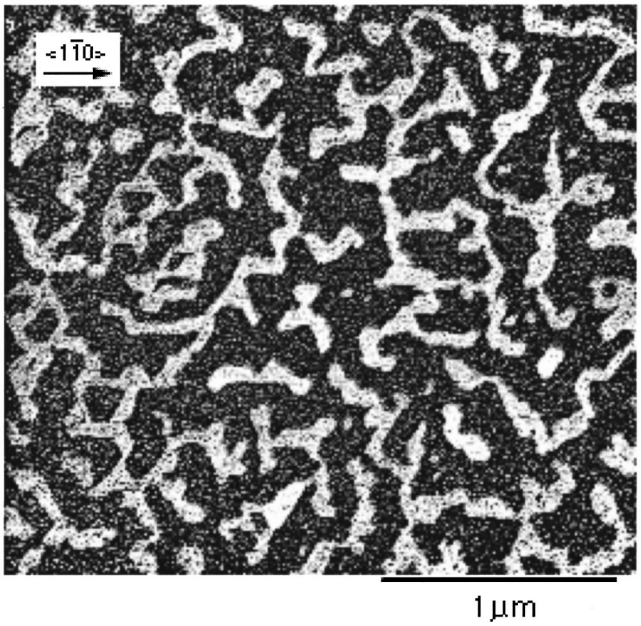


FIG. 4. SEM image of the $CoSi_2$ precipitate network formed upon agglomeration by heating the film up to 700 °C for 3 min. The arrow shows the direction of the Si(111)7×7 terraces exposed upon film agglomeration.

The dewetting process of the Si surface from the silicide film during high temperature annealing shows a rather complex aggregate structure which implies the possibility of two-dimensional fractal analysis. A simple way to measure the fractal dimension of a two-dimensional object is the box counting technique.[19] The image in Fig. 4 is digitized and

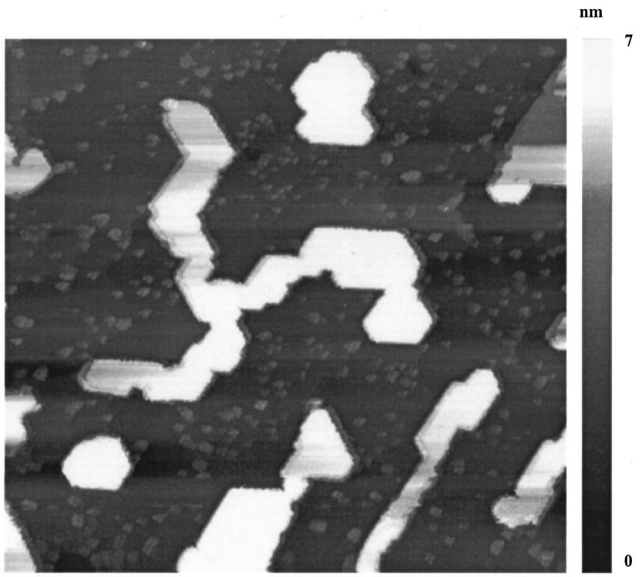


FIG. 5. Development of polygonal $CoSi_2$ precipitates with further annealing at 900 °C for 1 min (scan size 800×800 nm). STM empty state images of bias voltage 2.07 V and tunnel current 0.54 nA taken at different places on the sample.

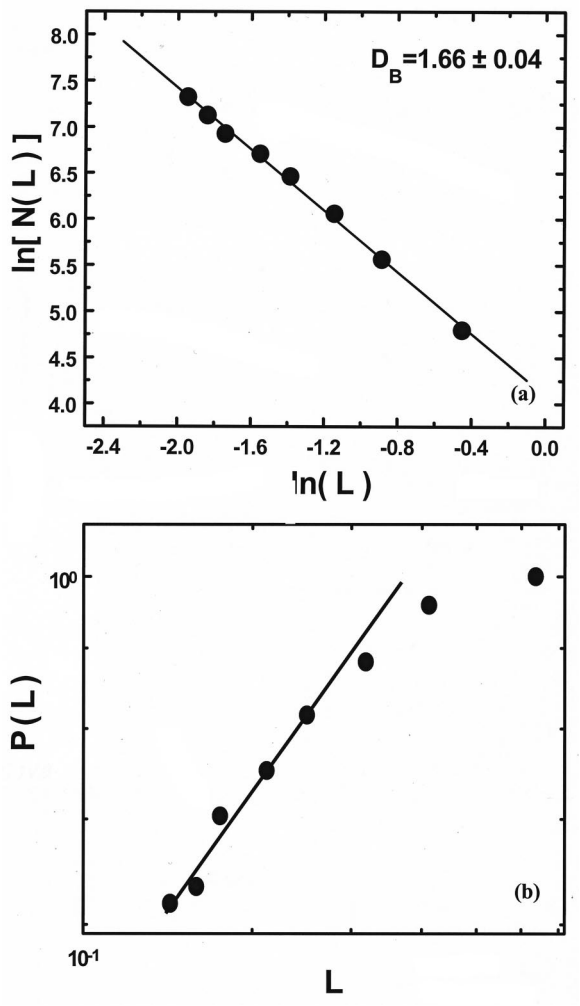


FIG. 6. (a) Measurement of the box counting fractal dimension as obtained from the line slope in the log–log of occupied boxes vs box size $L$. (b) Probability distribution of box occupation $P(L)$ vs the box length of size $L$. The line fit gives the slope $0.5\pm0.05$ which is the power law of $P(L)$.

covered with grids of varying box size of length $L$. If part of the $CoSi_2$ precipitates intersects a box from the grid, then the box is considered occupied by the aggregate complex. Plotting the number of occupied boxes $N(L)$ vs $L$ we obtain a power law behavior of the form[19]

$$N(L)\propto L^{-D_B}, \tag{1}$$

with $D_B$ the box counting fractal dimension. The linear fit in Fig. 6(a) yields $D_B=1.66\pm0.04$. If we denote by $A$ the image area, then the total number of grid boxes of size $L$ covering the image is $N^*=A/L^2$. Thus, the probability $P(L)$ of a box of size $L$ to be occupied by the aggregate is $P(L)=N(L)/N^*\propto L^{2-D_B}$. As is shown in Fig. 6(b), at small box sizes $P(L)$ shows a power law behavior $P(L)\propto L^{0.5\pm0.05}$ which is close (within the experimental uncertainty in the exponents) to the scaling relation $P(L)\propto L^{2-D_B}$. $P(L)$ at large box sizes saturates to the value 1.[20]

The dewetting behavior of the Si surface from the $CoSi_2$ face shows qualitatively features observed within the framework of the invasion percolation model. Indeed, such models were developed originally to study the slow displacement of a wetting fluid by a nonwetting fluid in porous media.[19] Computer simulations[21] gave for invasion percolation with trapping sites a fractal dimension $D_>=1.81$ above the percolation threshold and $D_{per}=1.37$ at the percolation threshold. In addition, simulations of diffusion limited aggregation (DLA) in two-dimensional networks gave fractal dimensions of $D_{DLA}=1.6-1.7$.[22] Indeed, the measured fractal dimension coincides with the mean field theory (in the sense that the strongly fluctuating but strongly correlated cluster density in a random fractal is replaced by a radial average) prediction for DLA growth,[19,22] namely,

$$D=(d^2+1)/(d+1), \tag{2}$$

which for a two-dimensional aggregation (or $d=2$) yields $D=1.66$. Despite the uncertainties concerning the asymptotic scaling structure for $d=2$, the value predicted by Eq. (2) may eventually be shown to be correct for DLA growth.[19] Note that the mean field theory prediction for DLA [Eq. (2)] gives the correct result for $d=1$, and satisfies the limit $D\geqslant d-1$ for $d\to\infty$.[19]

## V. CONCLUSIONS

We have investigated morphology changes of thin solid-phase-epitaxy $CoSi_2$/Si(111)$7\times7$ films close to agglomeration. The annealed films below the agglomeration threshold ($\sim$600 °C) reveal a strong morphology anisotropy, where depending on direction, the roughness correlation alternates from logarithmic ($\sim\ln r$) to power law ($\sim r^{2c}$ with $c\approx0.78$) at short lateral length scales ($r<30$ nm). Such a morphological anisotropy reflects to a significant degree the anisotropic nature of the diffusion process, because of the original anisotropic Si surface, that lead to formation of a pinhole network, and result in the more energetically stable Si-rich $CoSi_2$ surface. Annealing above the agglomeration threshold (>600 °C), the pinhole network becomes connected breaking the Co–silicide film into aggregates with a two-dimension fractal dimension $D_B=1.66$. Such a value resembles fractal characteristics close to those of invasion percolation and diffusion limited aggregation models. Indeed, $D_B\approx1.66$ lie between the invasion percolation model prediction $D_{per}<D_B<D_>$, as well as is very close to DLA model predictions $D_B$ ($\approx D_{DLA}$; especially within the framework of the mean field theory DLA approach). The later indicates a scenario that might describe such a complex agglomeration process. Further studies are required in this direction.

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[1]R. T. Tung, Metals Chem. Phys. **32**, 107 (1992); H. von Känel *et al.*, Appl. Surf. Sci. **53**, 196 (1991).
[2]Y. Yamaguchi *et al.*, IEEE Trans. Electron Devices **39**, 1179 (1992); H. Ronkainen *et al.*, IEEE Electron Device Lett. **12**, 125 (1991); S. Parekh *et al.*, IEEE Trans. Electron Devices **38**, 88 (1991).

[3]R. T. Tung and F. Schrey, Appl. Phys. Lett. **67**, 2164 (1995).
[4]K. Maex, Mater. Sci. Eng., R. **R11**, 53 (1993).
[5]T. P. Nolan *et al.*, J. Appl. Phys. **71**, 720 (1992); Z. G. Xiao *et al.*, Mater. Res. Soc. Symp. Proc. **202**, 101 (1991).
[6]B.-S. Chen and M.-S. Chen, J. Appl. Phys. **74**, 1035 (1993). The surface energies of $CoSi_2(111)$, $CoSi_2(220)$, and $CoSi_2(400)$ are, respectively, 2380, 2920, and 4130 erg/cm$^2$, while the surface energy of Si(100) is about 2300 erg/cm$^2$. See also T. Takai, T. Halicioglu, and W. A. Tiller, Surf. Sci. **164**, 341 (1985).
[7]L. E. Murr, *Interfacial Phenomena in Metals and Alloys* (Addison-Wesley, Reading, MA, 1975), pp. 122–135.
[8]B. Y. Tsui *et al.*, IEEE Trans. Electron Devices **40**, 54 (1993); T. P. Nolan *et al.*, J. Appl. Phys. **71**, 720 (1992).
[9]F. M. d'Heurle and C. S. Peterson, Thin Solid Films **128**, 283 (1985).
[10]G. Palasantzas, J. Appl. Phys. **81**, 246 (1997).
[11]The epitaxial argument is still under investigation, since SEM observations indicated a uniform retardation of film agglomeration (see also Ref. 6).
[12]H. Jones, Met. Sci. J. **5**, 15 (1971).
[13]B. Ilge, G. Palasantzas, L. J. Geerligs, and J. M. M. de Nijs, Surf. Sci. **414**, 279 (1998).
[14]Z. X. Xiao, G. A. Rozgonvi, C. A. Canovai, and C. M. Osburn, J. Mater. Res. **7**, 269 (1992).
[15]L. Ruan and D. M. Chen, Appl. Phys. Lett. **72**, 3464 (1998).
[16]G. Palasantzas, Phys. Rev. B **48**, 14472 (1993); **49**, 5785 (1994). The logarithm is obtained from the power law by means of the identity $\ln(x)=\lim_{c\to 0}(1/2c)[x^{2c}-1]$.
[17]P. Meakin, Phys. Rep. **235**, 1991 (1994); J. Krim and G. Palasantzas, Int. J. Mod. Phys. B **9**, 599 (1995); F. Family and T. Viscek, *Dynamics of Fractal Surfaces* (World Scientific, Singapore, 1991); G. Palasantzas and J. Krim, Phys. Rev. Lett. **73**, 3564 (1994).
[18]R. T. Tung and J. L. Bastone, Appl. Phys. Lett. **52**, 648 (1988); R. Stadler, N. Onda, H. Sirringhaus, H. von Känel, and C. W. T. Bulle-Lieuwma, J. Vac. Sci. Technol. B **9**, 2307 (1991).
[19]P. Meakin, in *Fractal, Scaling and Growth Far From Equilibrium* (Cambridge University Press, Cambridge, 1998). See pp. 303–304 on the mean field theory prediction given by Eq. (2).
[20]K. Radermacher *et al.*, J. Appl. Phys. **68**, 3001 (1990); A. H. V. Ommen *et al.*, Appl. Surf. Sci. **38**, 197 (1989).
[21]See Ref. 19, pp. 231–234.
[22]See Ref. 19, p. 258. See also P. Meakin, in *On Growth and Form*, edited by H. E. Stanley and N. Ostrowsky (Martinus Nijhoff, Boston, MA, 1986, pp. 120–121.; M. Muthukuman, Phys. Rev. Lett. **50**, 839 (1983); M. Tokoyama and K. Kawasaki, Phys. Lett. A **100**, 337 (1984).